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Electrochemical characterization of the passive films formed on niobium surfaces in H_2SO_4 solutions

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Abstract: The electrochemical formation and characteristics of passive films on niobium surfaces in aqueous H_2SO_4 solutions were studied using open circuit potential and cyclic voltammetry. In the potential region between –1.0 and 1.2 V (NHE), the cyclic voltammetry data showed that the active/passive transition involves slow metal dissolution followed by the formation of semiconducting passive oxide films. The possible electrochemical reactions and the change of the oxidation steps of some niobium oxides occurring in the passive film during the polarization are proposed. A strong influence of the natural air-formed oxide film on the chemical composition of the passive film was shown. This influence makes chemical structure of thin passive films more complicated than that of thick anodic films. It is shown that the passive films consists of more or less stable oxides, such as NbO, NbO_2 and Nb_2O_5. The Raman spectra revealed that the thin passive films were amorphous, while the films formed at higher voltages consist, primarily, of well-crystallized Nb_2O_5.

Keywords: niobium, passive films, open circuit potential, cyclic voltammetry, Raman spectroscopy.

INTRODUCTION

Over recent years there has been a growing interest in Nb and its alloys for use in the chemical industry (construction of chemical plants), mechanical industry (construction of high pressure transmission pipelines) and electrical industry (construction of super-conductive magnets). Nb has the highest transition temperature (9.3 K or –264 ºC) and among metals it is the most practical choice for super-conducting applications. Moreover, Nb also possesses high corrosion resistance due to its ability to spontaneously form stable passive oxides in air and aqueous solutions. The thickness of these films is 2 – 4 nm and it is extremely difficult to remove them from the metal surface.

The corrosion resistance of Nb can be enhanced by electrochemical formation of passive and/or anodic oxide films on its surface.[1–3] Most authors agree that the

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electrochemical formation of passive films on the surface of Nb in aqueous media yields an oxide of uniform thickness with an amorphous structure.[4–6] However, there is still great disagreement in the literature concerning the chemical structure of passive films especially the chemical composition of thin and thick films. The known stable oxides of Nb are: NbO, NbO_2 and Nb_2O_5. For Nb handled in air at room temperature, the sequence of chemical composition of dry natural oxide films, determined with modern surface spectroscopy techniques (XPS and AES), is an outermost layer (< 2 nm) of Nb_2O_5 over an NbO inner layer (< 1 nm). In some cases, an NbO_x ($x = 2$) layer (1–3 nm) has been also detected.[7]

In order to eliminate the presence of a natural oxide film and to commence their electrochemical experiments with a bare metal surface, Alkin *et al.*[4] mechanically polished the electrode surface in the usual way and then mechanically polished it in the solution under cathodic polarization. Different shaped voltammograms were registered, but is not clear what kind of oxide and how much of the natural oxide film had been reduced under the cathodic polarization.

Hitherto, relatively less attention has been paid to the influence of cathodic pre-treatment of a Nb electrode on the chemical composition of the passive films during anodization. The goal of this work was: (a) A more systematic study of the influence of cathodic pretreatment on the chemical composition of the initial anodic thin film formed on an Nb electrode; these studies were carried out by cyclic volatmmetry. (b) The determination of the chemical composition and crystallinity of the passive and anodic oxide films in dependence on the applied voltage; these studies were carried out by Raman spectroscopy.

EXPERIMENTAL

Electrodes

The working electrode consisted of an annealed 99.8 % niobium rod, 6.35 mm in dia, Alfa Aesar – Johnson Matthey Company. The Nb discs were embedded in epoxy resin (Struers) to offer an electrode with an exposed surface area of 0.316 cm^2. For determining which kind of surface preparation gives more reproducible voltammograms, mechanical, chemical and electrochemical polishing were utilized. In the first case, the electrode surface were stepwise mechanically polished with different grades of emery papers (from 400 to 5000) and then mirror polished with diamond sprays (from 6 to 0.1 μm). Chemical polishing was performed with mechanically polished electrodes which were dipped for 30 s in a solution contianing 5:3:1 in volume H_2O, HNO_3 and HF. In the third case of surface preparation, electrodes mechanically polished with emery paper 600 were electropolished at 15.2 V in a bath consisting of 170 ml HNO_3 + 50 ml HF + 510 ml CH_3OH + 5 g citric acid and vigorous stirring for 1 min at –5 ºC.[8] Finally, in all three cases of surface preparation, the electrodes were carefully rinsed with distilled water and ultrasonically degreased in acetone and ethanol.

A Pt grid with a large surface area and a saturated calomel electrode (SCE) were used as the counter and reference electrode, respectively. All the measured potentials are referred to the normal hydrogen electrode (NHE).

Electrochemical cell

A classical three-compartment cylindrical electrolytic cell equipped with Luggin capillary and an inlet and outlet for bubbling inert gas was used. The solution in the cell was initially de-aerated by argon flowing through a fritted bubbler for at least 30 min prior to the run. The gas flow through the solution was disconnected and argon was passed above the solution during the run.

Solutions

Aqueous solutions of sulfuric acid with concentrations of: 0.1 M, 1 M, 2 M, 5 M and 10 M were prepared by diluting concentrated H_2SO_4, (Merck, extra pure) with triply distilled water. The electrolyte in the cell was exchanged after each measurement, in order to avoid an eventual build up of soluble Nb species.

Apparatus

The electrochemical measurements were performed using a HEKA model 488 potentiostat/galvanostat connected with a personal computer. The Raman spectra were recorded on a "Renishow Ramanscope", utilizing red laser 633 nm. The laser power was diminished to only 1 mW in order to eliminate any surface perturbation from laser interaction.

RESULTS

Open circuit potential (OCP)

After the usual mechanical, chemical or electrochemical polishing, the Nb samples were immediately immersed in the aqueous H_2SO_4 solution and the OCPs were recorded. For all three kinds of surface preparation (mechanical, electrochemical and chemical polishing), the OCP shifted anodically with time (from about –750 to about –400 mV), obtaining parabolic shapes. The stabilization of the OCP as a result of self-passivation processes displayed the largest shifts of about 250 mV in the first 20 min, and during the measurement time of 200 min, only a part of the NbO_2 in the oxide film formed naturally on the Nb electrode was oxidized to Nb_2O_5. This self-passivation process shows good reproducibility of the recorded curves for the mechanically and electrochemically polished electrodes, while, for the chemically polished ones, a noticeable potential fluctuation was observed, probably due to the participation of some additional, as yet not defined, side reactions.

Cyclic voltammetry

In order to investigate the first instants of anodic film formation, three kinds of cyclic voltammetry measurements of freshly prepared Nb surface were performed: (*i*) starting from the steady state OCP after conditioning of 30 min in the solution; (*ii*) starting from a cathodic potential of –1.0 V and (*iii*) starting after cathodic pre-treatment at –1.0 V for 15 min. At low sweep rates, the cyclic voltammograms showed poor active/passive transition, regardless of whether the surface had been prepared by mechanical, chemical or electrochemical polishing. At faster sweep rates, the active/passive region for the rough mechanically polished (emery paper 400), and electrochemically polished electrodes was more pronounced and the voltammograms were satisfactorily reproducible. For the fine mechanically polished Nb electrodes (diamond spray 1 μm), even at a sweep rate of 200 mV/s, the active/passive region was still poorly defined, while the voltammograms for the chemically polished electrodes were less reproducible. For this reason, further measurements were performed only on rough mechanically polished and electropolished surfaces. These two kinds of surface preparation, for measurements starting from the OCP (approximately –450 mV NHE) and for measurements starting from a cathodic potential of –1 V gave voltammograms of similar shapes for the active/passive transition and for the values of the first passivation potential.

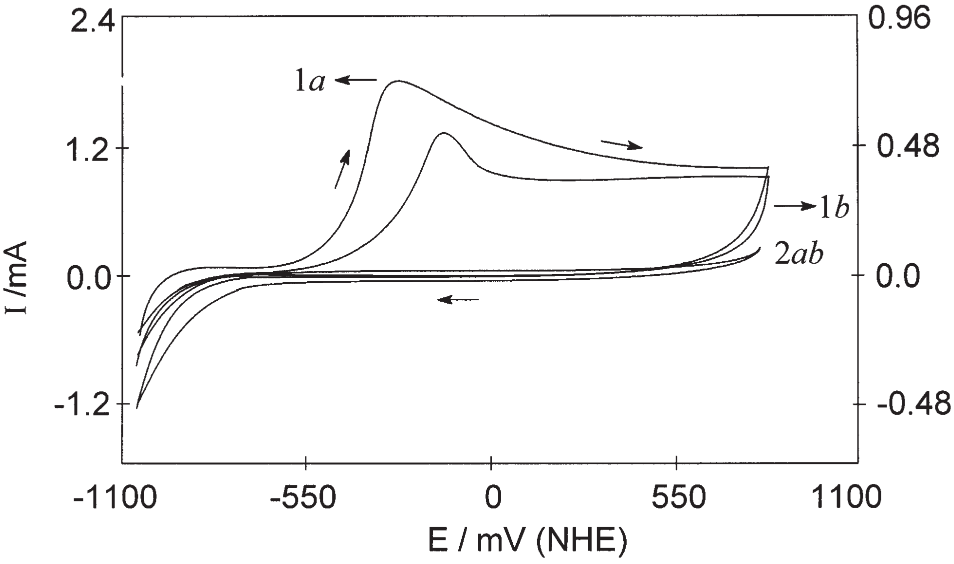

Fig. 1. Cyclic voltammograms of Nb electrodes recorded in 1 M H_2SO_4 starting from a cathodic potential of –1 V (NHE): 1a – first cycle of a mechanically polished electrode (400), 1b – first cycle of an electrochemically polished electrode, 2ab – second cycles for both electrodes (ν = 200 mV/s).

The voltammograms recorded on mechanically and electrochemically polished Nb surfaces, starting from a cathodic potential of –1.0 V, immediately after immersion of the electrodes in the elecytrolyte, are presented in Fig. 1. For both electrodes, in the first forward cycle only, one anodic peak appeared, the currents were much higher for the mechanically polished surface, and the active/passive transition was more pronounced for the electropolished surfaces. In the first reverse scan up to –1.0 V, at which potential hydrogen evolution or its intercalation in the electrode surface occurs, no cathodic peak was observed. It can be concluded that the passive films formed in the first positive scan cannot be cathodically reduced in the reverse scan. In the second cycle (curve 2ab), a constant current close to zero, for both the forward and reverse scans, was recorded. The voltammograms in the subsequent cycles were almost identical to the second ones. It is evident that, after the first cycle, the Nb electrode remained passive over the whole investigated potential range and the formed passive films blocked all possible redox reactions at the Nb/passive film/electrolyte interface.

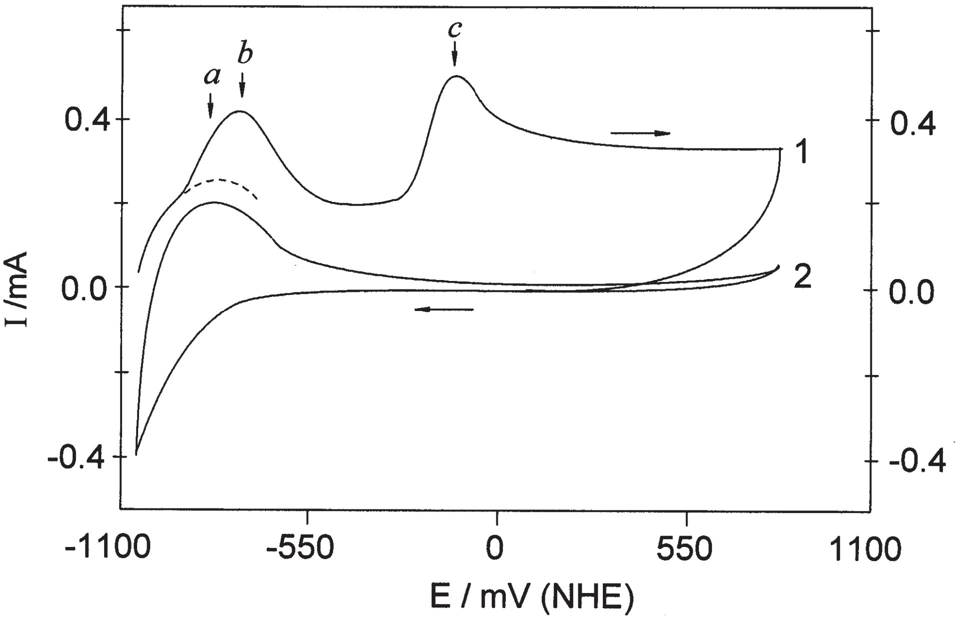

Fig. 2. Cyclic voltammograms of an electropolished Nb electrodes recorded in 1 M H_2SO_4 starting with cathodic pre-treatment for 15 min at –1 V (NHE): 1 – first cycle, 2 – second cycles recorded immediately after the first one (ν = 200 mV/s).

The next cyclic voltammetry measurements were carried out on mechanically and electrochemically polished Nb surfaces, with conditioning at the cathodic potential of –1.0 V for 15 min before the run. With strong stirring before the run, all the eventually adsorbed hydrogen bubbles were removed from the electrode surface. The first and the second cycles of the mechanically polished Nb surface showed voltammogrames with similar shapes to those shown in Fig. 1, but for the electropolished Nb surface, Fig. 2, dramatical changes in the voltammograme shape were observed. Two overlapping anodic peaks (a) and (b), and one well-defined peak (c) appear in the first positive scan. The corresponding cathodic peaks were not observed in the reverse scan. In the second cycle, only one anodic peak, corresponding to the overlapping peak (a) in the first scan, appeared. The third and the subsequent cycles (not presented in Fig. 2) had already the same shapes as the second one. It is evident that after the first cycle the peaks (b) and (c) disappeared. If, after multi cycle scans on the same electrode as in Fig. 2, the cathodic pre-treatment is again performed at –1.0 V for 15 min, the re-treated electrode showed the first cycle voltammogram given in Fig. 3. The shape and current densities of peaks (a) and (b) in this voltammogram are almost identical to those in Fig. 2. Peak (c) is completely missing in the first and also in the subsequent cycles. However, the second and the subsequent cycles of this electrode gave voltammograms of similar shape to that of the second cycle in Fig. 2.

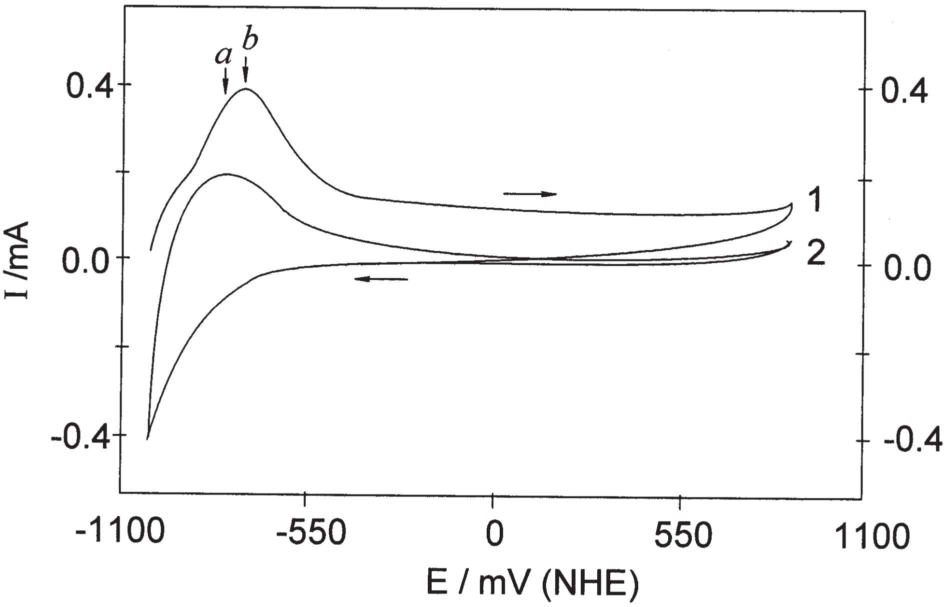

Fig. 3. Continued cyclic voltammograms on the same electrode from Fig. 2, after cathodic re-treatment for 15 min at –1 V (NHE): 1 – first cycle, 2 – second cycles recorded immediately after the first one (ν = 200 mV/s).

To re-obtain the anodic curve shown in Fig. 2 for the first cycle, it was necessary to re-new the electrode surface by re-polishing it. It is also not possible to re-obtain this anodic curve by simply submitting the electrode to cathodic polarization. This clearly shows that only some of the Nb oxides present in the passive film can be cathodically reduced.

The influence of the H_2SO_4 concentration on the corrosion resistance

Corrosion resistance of Nb was investigated in H_2SO_4 solutions of varying concentrations. The polarization measurements were performed within the range of –300 to +300 mV from the corrosion potential. The corrosion currents were determined from the Tafel plots and from the Stern–Geary equation using polarization data within – 20 and + 20 mV from corrosion potential. These measurements were carried out only for the rough mechanically polished surface (400), where the active region (in the potential range +300 mV from corrosion potential) corresponds to the dissolution of the metallic state Nb(0) to Nb(V) species.

$$2Nb + 5H_2O \rightarrow Nb_2O_5 + 10H^+ = 10e^- \qquad (1)$$

For the electropolished Nb surfaces, it is more complicated to determine the corrosion rate because in the active region many oxidation steps of Nb and Nb oxides are present (see reactions 2, 3 and 4 in the Discussion).

The representative examples of the Tafel plots of Nb in H_2SO_4 are given in Fig. 4. For all the investigated concentrations from 0.1 to 10 M H_2SO_4, the catho-

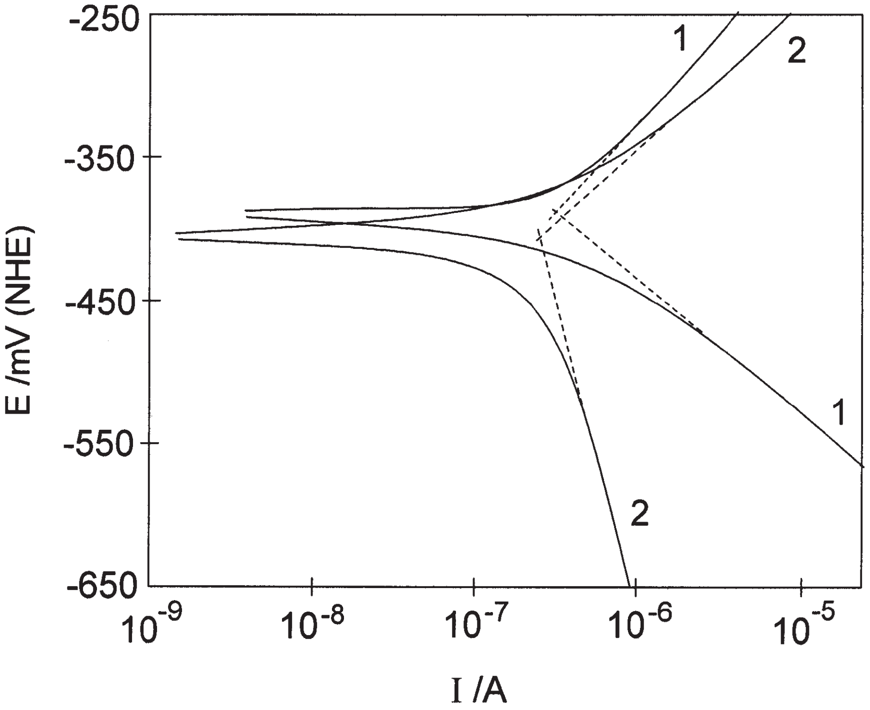

Fig. 4. Tafel plots of mechanically polished Nb surfaces recorded in: 1 –1 M H_2SO_4, 2 – 5 M H_2SO_4 (ν = 1 mV/s).

dic and anodic polarization curves followed almost linear Tafel behavior, resulting mainly from hydrogen evolution and metal dissolution. The corrosion currents, derived from the intersection of the extrapolated cathodic and anodic Tafel lines, slowly increase with increasing concentration of H_2SO_4. The corrosion parameters derived from the Tafel plots and corrosion resistance measurements are given in Table I. The high resistance values indicate the barrier properties of the passive films. From the corrosion data given in Table I, it can be concluded that the corrosion parameters change slightly between 0.1 and 10 M H_2SO_4 and that Nb is well-resistant even in higher concentrations of H_2SO_4. This resistance is ascribed to the natural oxide film and the supplementary formation of a passive film during the polarization. Apparently the passivation layer is electrochemically very stable.

TABLE I. Corrosion parameters of mechanically polished Nb surfaces in various concentrations of H_2SO_4

$c(H_2SO_4)$/mol dm^{-3}	j_{corr}/μA cm^{-2}	R_p/kΩ cm^{-2}	Corr. rate/μm year^{-1}
0.1	1.21	282	8.6
1.0	1.43	246	10.0
2.0	1.49	223	10.6
5.0	1.55	199	11.0
10.0	1.62	148	11.5

Raman spectroscopy

Raman spectroscopy has the great advantages of being a non-destructive method for the analysis of surfaces. The highly characteristic vibration stretching modes of the chemical bond allows composition identification.

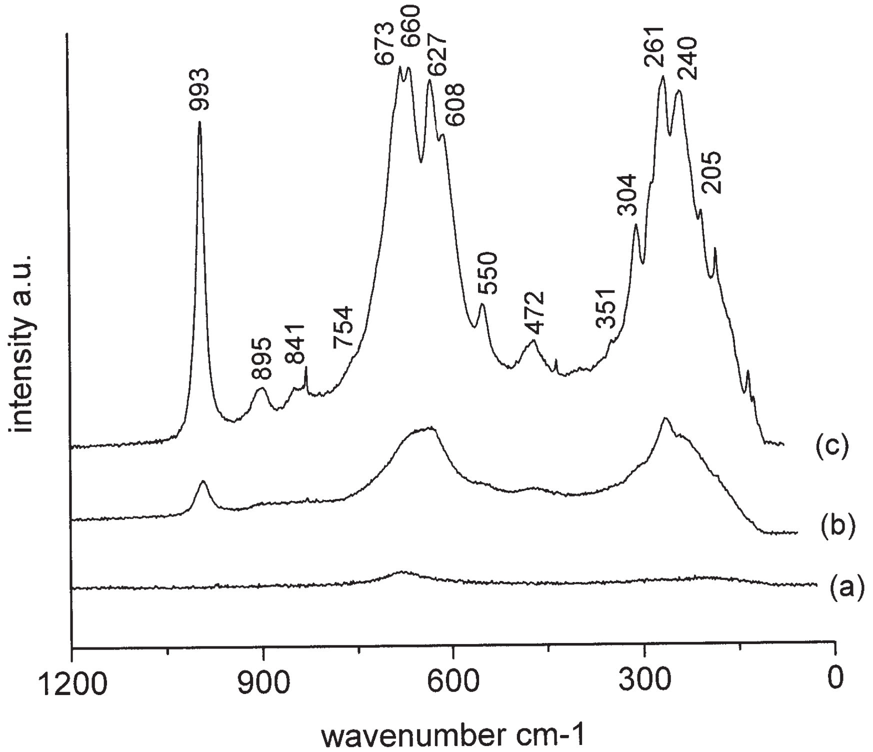

Fig. 5. Raman spectra of Nb anodicallly polarized in 1 M H_2SO_4: (a) – passive film formed at 1.2 V, (b) – anodic film formed at 150 V, (c) – Nb_2O_5 powder as a reference spectrum.

In this work, Raman spectra were recorded for thin passive and thicker anodic films formed on the surface of Nb in 1 M H_2SO_4. The assignments of the Raman bands were based on comparative measurements with reference niobium oxide compounds.

The Raman spectra of a passive film (a) and an anodic oxide film (b) are shown in Fig. 5. In the same diagram, the measured spectra of Nb_2O_5 powder (c), as the reference spectrum is also shown. For Nb surface with a natural air-formed oxide film, no active Raman bands appear, indicating the amorphous structure of this film. For the passive film formed at 1.2 V (NHE), two very broad bands, with maximums centered about 230 and 675 cm^{-1} can be hardly distinguished. The spectrum (b) was recorded for an anodic oxide film formed at 150 V. All the bands in spectrum (b) are located at the same wave number as the bands of the reference spectrum of Nb_2O_5 powder.

DISCUSSION

In the literature there is still a large discrepancy about the electrochemical properties and/or structure of the passive and anodic films formed at higher voltages on a Nb surface.[9–11] This discrepancy is more noticeable for thin passive than for thick anodic films, mainly due to participation of the NbO, NbO_2 and Nb_2O_5 from the naturally air-formed oxide film to the chemical composition of the thin film. Thus, during cycling, the redox reactions and transformations from one to another oxide or hydroxide form are more complicated in thinner films than in thicker films. The present investigations have shown that the surface preparation, the initial polarization conditions and various cathodic pre-treatments strongly affect the properties of the oxide film. In cyclic voltammetry measurements, electropolished Nb surfaces showed more reproducible voltammograms and more pronounced current peaks compared to mechanically polished ones. Mechanical polihsing or machining leaves numerous micro-scratches on the surface, which cause areas of different electrical potential due to surface stress. An electropolished surface has a more uniform potential distribution and because of this most of the present investigations were perforemd on electropolished Nb surfaces.

During cathodic pre-treatment of Nb for 15 min at –1.0 V, hydrogen ions diffuse from the electrolyte to the oxide film, probably forming a chemical bond with the oxygen of Nb_2O_5 in the natural oxide film:[12]

$$Nb_2O_5 + xH^+ + xe^- \leftrightarrows HxNb_2O_5 \tag{2}$$

Then, in the first positive scan, three anodic peaks at –790 mV, –745 mV and –120 mV could be identified. It is suggested that the first peak (a) in Fig. 2 corresponds to the formation of NbO, according to the reaction:

$$Nb + H_2O \leftrightarrows NbO + 2H^+ + 2e^- \tag{3}$$

The potential of Reaction (3) is in relatively good agreement with the Pourbaix diagram ($E\ = -\,0.733 - 0.0591$ pH). The second peak (b) corresponds to the oxidation of $HxNb_2O_5$ to Nb_2O_5 (the reverse direction of Reaction (2)), and the third peak (c) to the oxidation of NbO_2 to Nb_2O_5 following the reaction:

$$2NbO_2 + H_2O \rightarrow Nb_2O_5 + 2H^+ + 2e^- \tag{4}$$

Reaction (4) is irreversible and oxidation of NbO_2 from the natural oxide film produces Nb_2O_5, which is electrochemically stable. In the subsequent second and following cycles, the cathodic reduction of NbO and Nb_2O_5, according to Eqs. (3) and (2), were not observed, even at a low sweep rate. However, with cathodic re-treatment for 15 min at –1 V, the reduction of NbO to Nb and N_2O_5 to $H_xNb_2O_5$ occur and, consequently, two anodic peaks are recovered, as is shown on the voltammograms in Fig. 3.

Comparative analysis of our voltammograms with those previously published in the literature for cathodically pre-treated Nb surfaces shows good agreement with the anodic peaks (a) and (b) and the proposed reactions contributing in these two peaks.[4] However, in this paper, the voltammograms were recorded only up to – 0.45 V, hence the anodic peak (c) is missing. In addition, the potentiodynamic behavior of Nb_2O_5 and the corresponding redox reactions reported in Ref. 12 are in accord with the second and the subsequent voltammograms in the present experiments, where NbO_2 was eliminated by its oxidation to Nb_2O_5 (Reaction (4)).

Recently, Huang *et al.*[13] have demonstrated the facile formation of a stable passive film on Nb electrode in 0.15 M NaCl, as well as in 0.1 M NaOH. Starting from a cathodic potential (–1.3 V *vs.* Ag/AgCl), where the current density is substantial, their voltammogram in the first positive scan displays four anodic peaks. In the potential region from –1.3 to 1.4 V, they claimed the existence of four oxides: NbO, NbO_2, Nb_2O_5 and $Nb_2O_5\cdot nH_2O$. Their results are consistent with ours, but only for the first three anodic peaks. The existence of $Nb_2O_5\cdot nH_2O$ in this potential region was not electrochemically monitored from our side. These authors used the SERS effect of an Ag-coated electrode surface and also registered Raman active bands of Nb electrochemically treated in 0.15 M NaCl at – 0.4 V (OCP) and 0.4 V *vs.* Ag/AgCl. Their Raman spectra are generally weak with some ill-defined bands. They showed that the Raman spectrum of NbO_2 consists of only three bands; one of medium intensity, centered at 704 cm^{-1}, and two weak and broad bands, centered at 475 cm^{-1} and 392 cm^{-1}. The key band for distinguishing NbO_2 is the medium intense band at 704 cm^{-1}. This band was not observed in our spectrum for Nb anodically oxidized at 150 V. According to these authors, the passive film is composed of NbO_2 and different forms of Nb_2O_5, such as H–Nb_2O_5, N–Nb_2O_5 and B–Nb_2O_5. Some of their bands, deviate noticeable from the Raman bands of the reference spectra given in the literature. For the thicker anodic films, our Raman spectra show well-defined Raman bands, indicating a progressive increase it in the crystallinity of the film with the applied voltage. Comparing the spectra of our anodic oxide film and the reference spectra of powdered Nb_2O_5, it is evident that the anodic oxide film is composed of Nb_2O_5.

CONCLUSION

The present study has demonstrated the presence of various oxide forms of Nb in natural, passive and anodic films formed in H_2SO_4. The oxide films formed under atmospheric conditions consist of NbO, NbO_2 and Nb_2O_5. During polarization, NbO_2 is irreversibly oxidized to Nb_2O_5 and Nb is reversibly oxidized to NbO. The reversible redox reaction $Nb_2O_5/H_xNb_2O_5$ occurs only if the electrode surface was cathodically pre-treated at –1 V, for at least 15 min before the run.

The Raman spectra reveal the amorphous structure of natural and passive oxide films. The crystallization of the oxide film progressively develops with increasing anodic potential. In the anodic oxide films, only the Nb_2O_5 oxide form of niobium was registered.

Niobium surfaces with natural and passive films possess high corrosion resistance even in concentrated H_2SO_4 solutions.

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ИЗВОД

ЕЛЕКТРОХЕМИЈСКА КАРАКТЕРИЗАЦИЈА ПАСИВНИХ ФИЛМОВА НИОБИЈУМА ФОРМИРАНИХ У РАСТВОРИМА H_2SO_4

ИРЕНА АРСОВА, АБДУРАУФ ПРУСИ, ТОМА ГРЧЕВ и ЉУБОМИР АРСОВ

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Електрохемијска пасивација ниобијума у воденим растворима H_2SO_4 испитивана је помоћу цикличне волтаметрије у области потенцијала од –1 до 1,2 V (NHE). На волтамограмима се појављује област активног растварања метала и пасивна област у којој се формирају полупроводнички филмови од мање или више стабилних оксида као што су NbO**,** NbO_2 и Nb_2O_5. За време циклизирања потенцијала одиграва се реверзибилан редокс процес Nb/NbO и иреверзибилна оксидација NbO_2 до Nb_2O_5. Реверзибилна редокс реакција $Nb_2O_5/H_xNb_2O_5$ дешава се само ако се пре почетка цикличне промене потенцијала ниобиумова електрода катодно полазирује најмање 15 min на потенцијалу од –1 V (NHE). Велика стабилност пасивних филмова ниобијума, у опсегу концентрација од 0,1 M до 10 M H_2SO_4, потврђена је одређивањем корозионих параметара помоћу Тафелових дијаграма и поларизационе отпорности. Брзина корозије креће се у границама од 8,6 μm/god у 0,1 M H_2SO_4 до 11,5 μm/god у 10 M H_2SO_4. Рамановом спектрометријом показана је аморфна структура пасивних филмова, док са повећањем анодне поларизације, кристализација прогресивно напредује са повећањем дебљине формираног филма. Дебљи анодни филмови, добијени на 150 V, састоје се само од кристалне Nb_2O_5 фазе.

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